

Hydrogen Absorption in Electropolishing of Niobium

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Abstract. Electropolishing process had been considered to cause hydrogen absorption that could result in hydrogen Q-disease in niobium superconducting RF cavities. Recently, however, we found that hydrogen Q-disease did not always occur in a L-band niobium RF cavity treated by continuous electropolishing (EP) only.

We consider mechanical grinding as a very powerful method to eliminate surface defects. Therefore, our surface treatment process is a combination of mechanical grinding and EP. We developed a simple and fast mechanical grinding method, centrifugal barrel polishing method (CBP), as the pre-treatment for the EP. We applied a combination of CBP and EP to a L-band niobium cavity and found the result showing a heavy hydrogen Q-disease. We found out that hydrogen absorption occurred during the CBP, and the absorbed hydrogen came from the water used during the CBP. Hence, we replaced the water by a liquid without hydrogen as its component. As the result, we successfully prevented hydrogen absorption in the CBP. However, the combination of hydrogen-free CBP and EP resulted in a heavy hydrogen Q-disease again. The hydrogen might have been absorbed through surface defects caused by the CBP.

We found hydrogen Q-disease did not occur by the combination of hydrogen-free CBP and chemical polishing (CP). CP acid contains nitric acid functioning as an oxidiser. EP acid doesn't contain chemicals that function as oxidiser. This suggested that oxidation helps preventing hydrogen absorption. In the EP, oxidization occurs only when electric voltage is applied. There are moments during the EP, when electric voltage can not be applied (at the beginning and at the end), which in turn stops oxidation so that hydrogen absorption would occur. To assure the effect of the continuous oxidization, we put a small amount of nitric acid in the EP acid, and the additional oxidizer prevented hydrogen absorption successfully.

INTRODUCTION

Electropolishing (EP) needs equipments such as electrodes, current generator etc., and is more complicated than chemical polishing (CP). Recently, however, performance superiority of EP in superconducting niobium cavities was recognized. This means that an electropolished cavity sustains higher voltage gradients than chemically polished cavities [1]. Now, EP is becoming the standard surface treatment in the world.

It had been recognized that during the old intermittent EP process, hydrogen is absorbed into niobium cavity, and causes catastrophic Q degradation called “hydrogen Q-disease” [2]. During the TRISTAN R&D at KEK, continuous horizontal EP method was developed [2]. However, we had insufficient time to check, if hydrogen absorption would be induced by this new EP method. Annealing was applied to all the TRISTAN cavities to assure hydrogen-free cavities. Although the TRISTAN cavities reliably achieved high performance, the cost for their surface treatment was rather high. Considering a large-scale mass production of superconducting cavities for TESLA for example, development of reliable and cost effective surface treatment method is a key issue. If the hydrogen absorption could be prevented in the surface treatment, annealing process would be omitted resulting in a considerable saving in both cost and processing time.

To develop a hydrogen-free process, we studied the relation between EP and hydrogen Q-disease. Using a new 1300MHz (L-band) niobium single-cell cavity with RRR (Residual Resistivity Ratio) = 200, we checked, if the hydrogen Q-disease would be induced by the TRISTAN style EP. Hydrogen Q-disease was not observed after removing approximately 200 μ m from the surface as shown in FIGURE 1 [3]. This was unexpected, since we did not apply annealing. To further investigate the mechanism of hydrogen absorption during EP, we studied several ways of doing EP. Applying electric voltage continuously to the samples during the EP reduced hydrogen absorption [3]. We also observed hydrogen absorption in a niobium sample that went through centrifugal barrel polishing (CBP) only [4]. This fact motivated us to the further study of the hydrogen absorption mechanism during CBP. At the end, we understood it and established a hydrogen-free CBP using a hydrogen-free polishing liquid, FC-77.

We combined the hydrogen-free CBP and the continuous EP. This resulted a heavy hydrogen Q-disease to our surprise. We found that defects made by the CBP caused

hydrogen absorption during the following EP. On the other hand, hydrogen absorption was not observed in the combination of the hydrogen-free CBP and CP. The difference between the EP and CP lies in the polishing liquid; CP has an oxidation power and EP does not. This suggested that continuous oxidation is a key for hydrogen-free surface treatment process. We invented a new EP acid by adding oxidizer to it and hydrogen Q-disease problem was completely resolved.

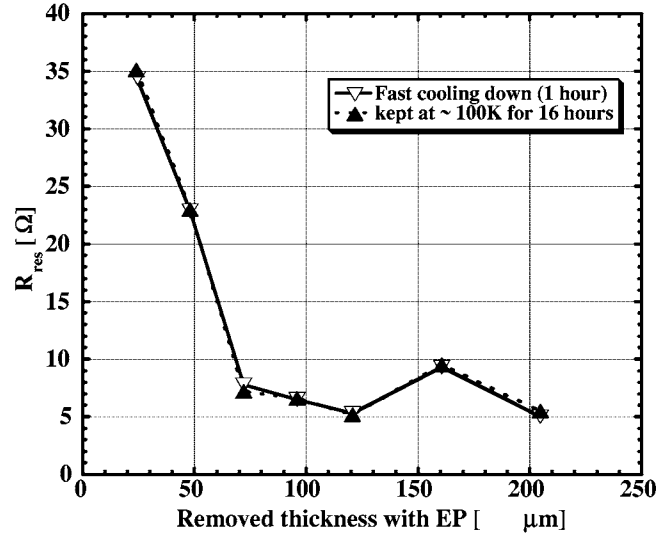


FIGURE 1. No Hydrogen Q-disease with massive 200 μm material removal with EP.

EXPERIMENTAL

Evaluation of Hydrogen Q-disease

The unloaded Q-value (Q_0) of a cavity is inversely proportional to the surface resistance R_s of the cavity (under the condition that $T \leq T_c/2$):

$$Q_0 = \frac{\Gamma}{R_s}, \quad \Gamma = 273 \, \Omega. \quad (1)$$

$$\begin{aligned} R_s &= R_{BCS} + R_{res} \\ &= A \cdot \frac{\omega^2}{T} \cdot \exp\left[-\frac{\Delta_0}{k_B T}\right] + R_{res}. \end{aligned} \quad (2)$$

where Γ is a constant that depends on a cavity shape and is 273Ω for our L-band cavity. For superconducting cavities, R_s consists of two terms: theoretical BCS surface resistance R_{BCS} [5] and residual surface resistance R_{res} that depends on surface contamination. A is a constant that depends on material, ω is the RF frequency, $2\Delta_0$ is the band gap energy of the superconductor, k_B is the Boltzmann's constant. T [K] is the temperature of the cavity. We can measure R_s , then calculate R_{BCS} and R_{res} by fitting the data (see FIGURE 2). The accuracy of the measurement of R_{res} was about $1n\Omega$ and typical value of R_{res} is $5n\Omega$ for a degassed cavity.

The degree of hydrogen Q-disease is dependent on the amount of absorbed hydrogen in the niobium material and on the time the cavity was exposed at the dangerous temperature region [6, 7]. Hydrogen Q-disease appears as the degradation of Q_0 value, corresponding to an increased surface resistance. We decided our evaluation procedure on the degree of hydrogen Q-disease. We defined the level of hydrogen disease as the change in R_{res} before and after exposing the niobium at the dangerous temperature range. Actual measurement was done as follows: First, cool down from 300K to 4.2K and then do the measurements of R_s 's. From these, we can find R_{res} (baseline measurement). Then the cavity was warmed up to 100K and kept there for 16 hours. After this, the cavity was cooled down to 4.2K and the second set of measurements of R_s 's for the second value of R_{res} was carried out.

An example of the hydrogen Q-disease is presented in FIGURE 2.

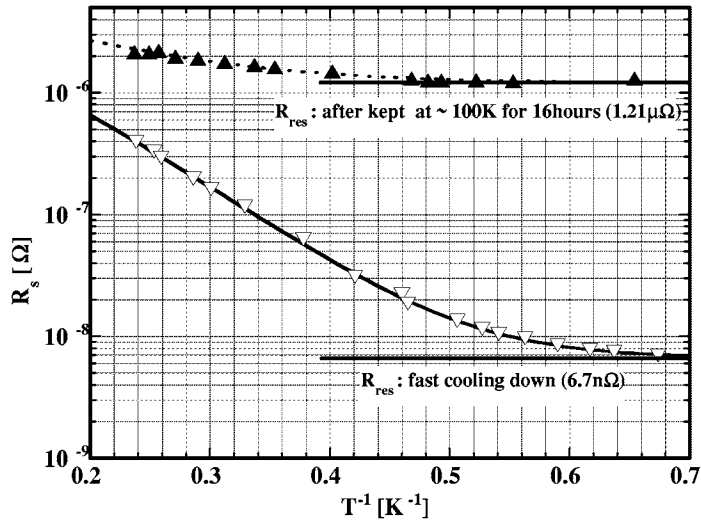


FIGURE 2. Measurement of residual surface resistance of a cavity

Measurement of hydrogen concentration in a niobium sample

Hydrogen concentration in test samples was measured by hydrogen gas chromatography by melting niobium samples. Data analysis was done by an outside lab, which used a hydrogen detector: LECO Co. Model RH-404. The measurement procedure is shown in FIGURE 3. In this method, the measured amount of hydrogen is the average of the whole sample.

For the sample preparations, we well degassed hydrogen from the material by annealing at 750°C for 5hrs at a pressure of 1×10^{-6} torr before the subsequent experiments. Thus the initial hydrogen concentration in the samples was less than 1ppm. When we applied CBP to samples, we did ultrasonic rinsing. After the surface treatment, we kept the samples in nitrogen gas atmosphere until measurement started. The accuracy of the measurement is 1 to 2ppm. We observed a good agreement between the degree of hydrogen Q-disease of a cavity and hydrogen concentration of test sample by the same treatment [3].

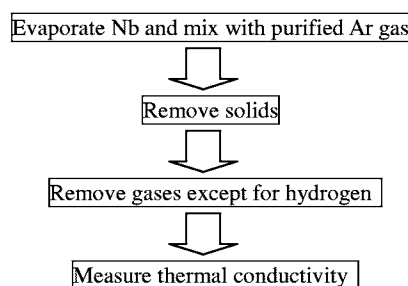


FIGURE 3. Measurement of amount of hydrogen in a niobium sample

RESULTS AND DISCUSSION

Hydrogen absorption during the CBP

To remove ambiguity in measuring the amount of absorbed hydrogen, all sample strips and cavities were annealed before the measurement. A cavity was treated by the combination of 30 μ m of CBP and 50 μ m of EP. For the CBP we used 2150g of GCT media 2150g immersed in 850cc water with detergent inside the cavity, rotating at 160rpm for 4hours. The result showed a heavy hydrogen Q-disease as seen in FIGURE 4. From this result and the previous test results in FIGURE 1, the CBP must

have induced hydrogen absorption. We put niobium samples (2.5mm x 1.0mm x 147mm, RRR = 200) in a cavity during the CBP process. We measured the hydrogen concentration in the samples. It was 78ppm. We thus confirmed that severe hydrogen absorption occurred by the CBP.

To understand the hydrogen absorption mechanism, we studied the effect of water used for CBP applied on niobium samples (2.5mm x 1.0mm x 147mm, RRR = 200). The result is shown in TABLE 1. In the case of water without detergent, the hydrogen concentration was 79ppm and no difference from our standard case, water and detergent mixed. The detergent thus has no effect on the hydrogen absorption. However, without the addition of water to the solid polishing media, the hydrogen concentration was reduced remarkably and was 11ppm. This confirmed that the absorbed hydrogen came from the water used in CBP.

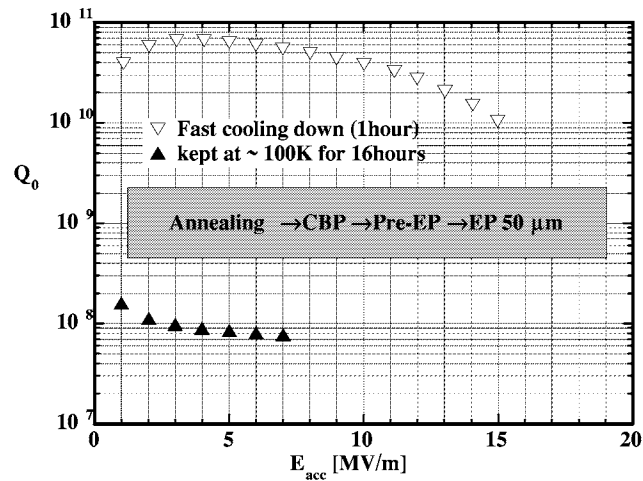


FIGURE 4. Heavy hydrogen Q-disease did occur in combination of CBP and EP

TABLE 1. Absorbed hydrogen during 4hours of various CBP

Liquid used in CBP	Hydrogen concentration in the test sample	Removed thickness from the cavity wall	Comments
Water and detergent	78.0 ± 2.9 ppm	30μm	Standard composition
Water	79.1 ± 5.0 ppm	29μm	No detergent
No liquid	10.9 ± 0.8 ppm	~0μm	Solid media only
Propanol	49.4 ± 2.2 ppm	31μm	No water
FC-77 (C_8F_{18} and $C_8F_{16}O$)	4.6 ± 0.8 ppm	20μm	No hydrogen
10% hydrogen peroxide	28.4 ± 1.4 ppm	24μm	Oxidation effect

(Measurement of hydrogen concentration was repeated ten times over each sample)

The above evidence suggests that damaged niobium surface during the CBP picks up hydrogen from water. If this assumption is correct, the amount of absorbed hydrogen will depend on liquid that was used during CBP. We compared water with propanol. Though the amount of absorbed hydrogen was reduced when the propanol was used, still a lot of hydrogen (60% of the water case) was detected. The best way is to use a hydrogen-free liquid. Fortunately we can commercially obtain such a liquid e.g. FC-77 (mixture of C_8F_{18} and $C_8F_{16}O$, a product of the 3M Co.). With the FC-77, hydrogen concentration was reduced dramatically and was 5ppm. Thus we found a hydrogen free CBP using a hydrogen-free liquid.

Combination of hydrogen-free CBP and EP

We expected the combination of the hydrogen-free CBP and EP would have solved the hydrogen problem. We applied this combination to a L-band cavity. Actual procedure involves the following: 1) after the hydrogen-free CBP, the cavity was rinsed with FC-77, 2) pre-EP was applied to remove only a micron from the surface. Surface finished with CBP is contaminated with dirt (niobium powder and medium powder). Without the pre-EP, the EP polishing liquid gets very dirty. Therefore we applied EP briefly without circulating the polishing solution and discarded the contaminated solution. 3) The following main EP removed 50 μ m thickness with the liquid circulating.

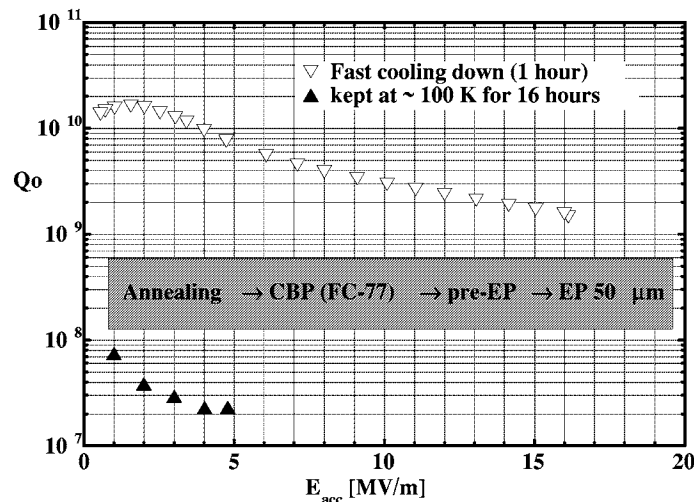


FIGURE 5. Heavy hydrogen Q-disease did occur when hydrogen-free CBP and EP were combined

We measured the cavity performance. The result showed a heavy hydrogen Q-disease as presented in FIGURE 5. This means the hydrogen-free CBP did not solve all the problems.

As already seen in FIGURE 1, hydrogen Q-disease didn't occur in the case, when only EP was applied to a cavity. Hence surface defects such as scratches made by the CBP are suspected to be the cause of hydrogen absorption in the subsequent EP. To confirm this, we applied the hydrogen-free CBP (for 4 hours) to niobium samples first. Then applied electropolishing to them in order to remove different thickness for different sample. Measured hydrogen concentrations in these samples are shown in FIGURE 6. We confirmed that hydrogen absorption occurred during the EP process after the hydrogen-free CBP.

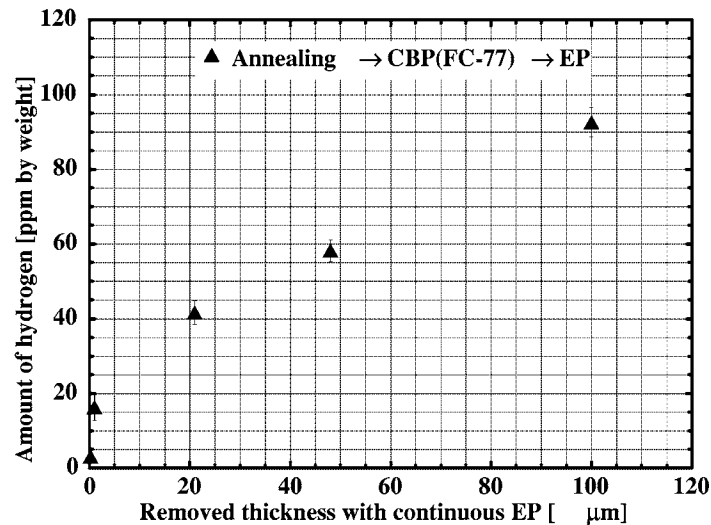


FIGURE 6. Hydrogen absorption occurred during EP that followed after the hydrogen-free CBP

Combination of hydrogen-free CBP and CP

To compare EP with CP, we treated a cavity with the combination of hydrogen-free CBP and CP. In this case, hydrogen Q-disease was not observed as shown in FIGURE 7. This was confirmed by hydrogen gas analysis on niobium samples as seen in FIGURE 8. While the amount of hydrogen was found to be very small, hydrogen was found to be located near the surface. No hydrogen was observed after removing more than 20μm. Now we found a hydrogen-free process by the combination of the hydrogen-free CBP and CP.

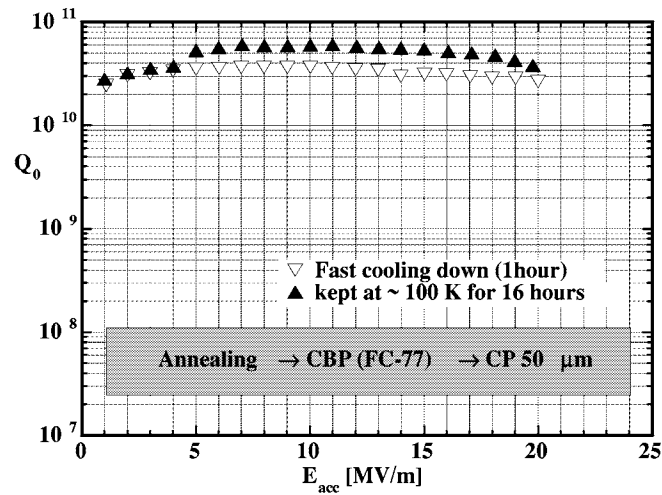


FIGURE 7. Hydrogen Q-disease did not occur with combination of hydrogen-free CBP and CP

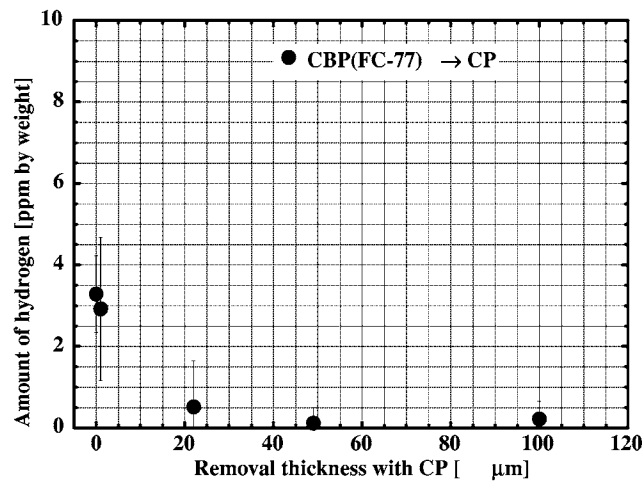


FIGURE 8. Hydrogen absorption didn't occur during CP that followed after hydrogen-free CBP

Results were different between the application of EP and application of CP after hydrogen-free CBP. What was the reason? Etching process progresses on oxidized metal in general. In CP, oxidation is achieved by the solution and in EP the oxidation is done through externally applied voltage. Our EP acid for niobium consists of hydrofluoric acid and sulfuric acid. CP acid consists of hydrofluoric acid, phosphoric

acid and nitric acid. Nitric acid is a powerful oxidizer. We considered that the continuous oxidation process of CP is the key to understand the difference. The effect of oxidation for hydrogen prevention can be seen in TABLE 1. When we used hydrogen peroxide instead of water in CBP, hydrogen concentration was reduced to 1/3. This could be due to the oxidation effect by hydrogen peroxide.

Combination of oxidizer-added CBP and EP

To see the effect of oxidation during CBP, we prepared test samples through applying CBP and EP where CBP liquid was FC-77 and ozone was bubbled through it (oxygen gas with 4% ozone for 20 minutes). This would provide the capability of oxidation in the liquid during CBP. With this addition of ozone, we could reduce the amount of absorbed hydrogen remarkably as seen in FIGURE 9.

We then applied this oxidizing CBP to a single-cell cavity. But the result was serious hydrogen Q-disease (FIGURE 10). So, we had to find out what caused the difference. One difference we could come up with was that we applied pre-EP before main EP for the cavity sample and no pre-EP for strip samples.

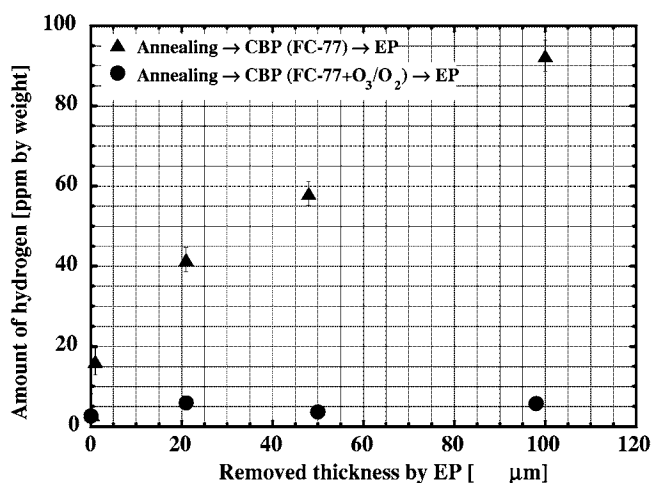


FIGURE 9. Hydrogen absorption during EP after oxidizing-hydrogen-free CBP

This implied two possible explanations for the difference. Since we did not circulate liquid to prevent dirt to circulate, this caused a significant temperature rise (to 37°C) in case for the cavity while it stayed below 31°C for strip samples.

Especially during pre-EP, the niobium will be exposed to the polishing liquid without external voltage which in turn means no oxidation action. We did simulation of the pre-EP with a strip sample (2.5mm x 1.0mm x 147mm, RRR=200) and hydrogen absorption was observed and amount of hydrogen was 16.7 ± 3.4 ppm.

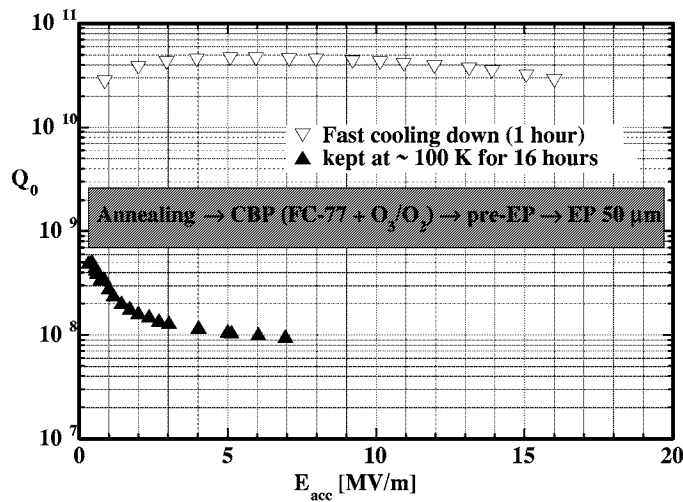


FIGURE 10. Heavy hydrogen Q-disease did occur after the combination of oxidizing CBP and EP

New EP acid

We found that adding oxidizer is effective to reduce hydrogen absorption. If we can add a capability of oxidation to EP solution, it might prevent the hydrogen absorption while the combination of the hydrogen-free CBP and EP is applied. We added a little of nitric acid to our EP acid (1500ppm) and applied EP on a cavity processed by hydrogen-free CBP prior to it. We measured performance of the cavity and hydrogen Q-disease was not observed as shown in FIGURE 11. Now we have developed the hydrogen-free treatment for EP. However, Q-slope (degradation of Q_0 value in the high field) was observed (FIGURE 11). This phenomenon has been often observed on cavities treated with CP. It might be caused by the added nitric acid.

To find out optimum amount of nitric acid that will be effective to prevent hydrogen Q-disease to occur, but not causing Q-slope, we did sample tests. After hydrogen-free CBP (GCT media 2150g, FC-77 850cc, 160rpm, 4 hours), we removed 100μm of material by EP using acid that contains various amounts of nitric acid (from 1500ppm to 15ppm). The result is shown in TABLE 2. In the sample test, even the

15ppm of nitric acid could prevent hydrogen absorption. We are preparing tests on sample strips to measure the amount of hydrogen absorption during pre-EP and tests on cavities to check if the Q-slope appears.

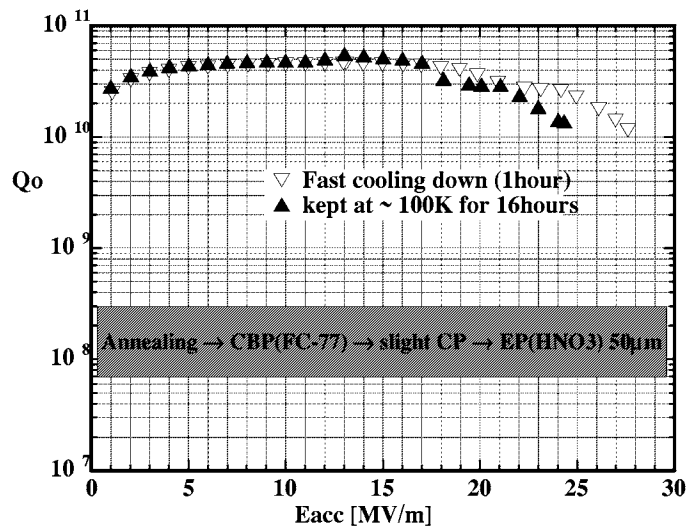


FIGURE 11. No hydrogen Q-disease resulted for combination of H-free CBP and oxidizer added EP

TABLE 2. Hydrogen absorption through a combination of hydrogen-free CBP and nitric acid-added EP

Concentration of nitric acid in EP acid	Hydrogen concentration	Removed thickness by nitric acid-added EP
1500 [ppm]	0.53±0.28 [ppm]	100
150 [ppm]	1.03±0.44 [ppm]	100
15 [ppm]	1.69±0.22 [ppm]	110

(2.5mm x 1.0mm x 147mm, RRR=200)

Discussion

Hydrogen Absorption on a Surface that had absorbed Hydrogen

We found that a combination of hydrogen-free CBP and CP is a hydrogen-free treatment process. The combination of hydrogen-free CBP and oxidizing EP is also one other hydrogen-free polishing process. However, if hydrogen had been absorbed prior to these polishing process, further absorption was induced during the following CP or EP (FIGURE 12 and 13). There are many reports from many laboratories about the occurrence of hydrogen Q-disease in cavities for which only CP had been applied.

We think that these happened, because the cavities had absorbed hydrogen prior to the CP, probably during fabrication process.

In one case, prior absorption of hydrogen could be successfully removed by EP but there was other case where hydrogen absorption progressed further through EP as seen in FIGURE 13.

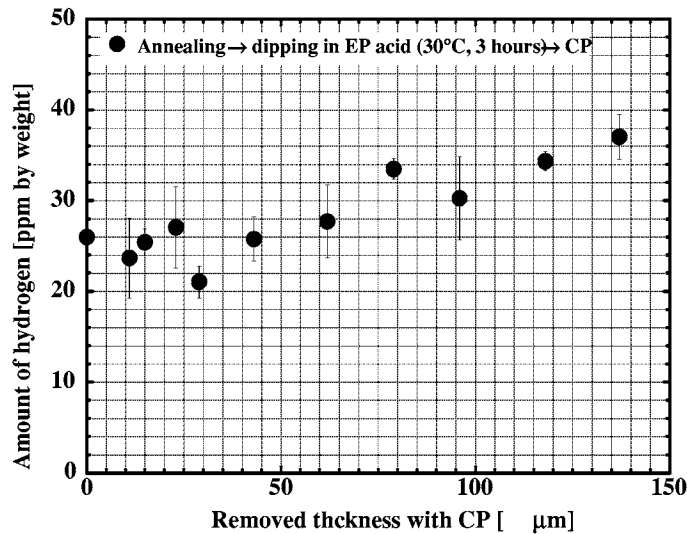


FIGURE 12. Once hydrogen absorption occurred in earlier stage, it will continue during CP

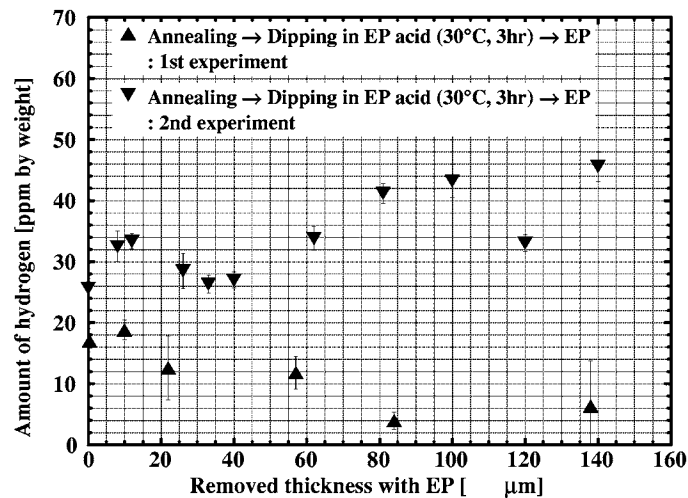


FIGURE 13. Hydrogen absorption during EP on niobium that had absorbed hydrogen

Hydrogen Absorption during EP or CP following Hydrogen-free CBP

In the combination of hydrogen-free CBP, hydrogen absorption occurs in EP (normal EP acid) and doesn't occur in CP. To study this difference, we developed a model as described below.

For the hydrogen absorption through surface defects, the followings could be assumed:

- 1) Most hydrogen is trapped on surface defects. Hence the number of hydrogen atoms is proportional to the number of defects.
- 2) The number of the surface defects made by mechanical grinding (CBP) decreases exponentially with the depth from the surface. Hence the number of defects decreases exponentially with the thickness from the surface removed by the following polishing.

For the absorbed hydrogen through grain boundaries (channeling effect) [8]

- 3) Hydrogen concentration will be proportional to the immersed time in the acid.

If we take into account only these mentioned above, the absorbed hydrogen concentration C as a function of the removed thickness could be expressed as follows:

$$C(x) = C_1 \cdot \exp\left[-\frac{x}{d}\right] + C_2 \cdot x. \quad (3)$$

where x is the thickness removed by following polishing after the hydrogen-free CBP, d is the depth of damaged surface layer. C_1 and C_2 are constants. Actually as shown in FIGURE 14, the CP data can be well fitted by this function with a damaged depth of 11 μm . This fact suggests that the hydrogen is trapped on defects only and doesn't enter to the bulk through surface defects.

However, this function doesn't fit the EP data well. The data can be well fitted by the integration of the exponential part in equation (3) and channeling effect as below:

$$C(x) = C_1 \cdot \int_0^x \exp\left[-\frac{t}{d}\right] dt + C_2 \cdot x = C_1 \cdot d(1 - \exp\left[-\frac{x}{d}\right]) + C_2 \cdot x. \quad (4)$$

These results suggest the followings;

- 1) Defects made by CBP are localized within about 10 μm from the surface, which corresponds to the surface roughness measured by an independent method ($R_z \sim 10\mu\text{m}$).
- 2) When hydrogen-free CBP was followed by CP, the hydrogen trapped on the surface defects during CBP can be removed by CP.
- 3) When hydrogen-free CBP is followed by EP, the hydrogen enters through surface defects and get into the niobium bulk.

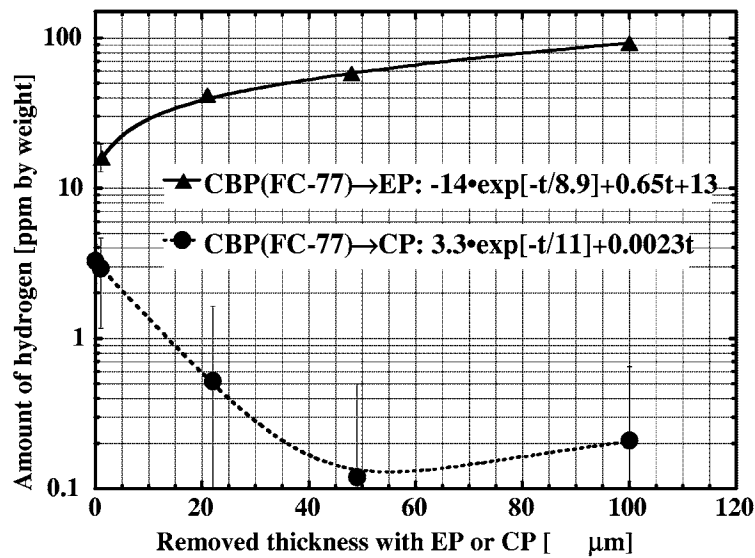


FIGURE 14. Hydrogen absorption during EP or CP that followed after hydrogen-free CBP

Application of the hydrogen-free chemistry

The results of this study could be applied to improve surface finishes of other materials such as components of ultra-high vacuum system because hydrogen gas is the main component of residual gasses in such a system. The understanding on the hydrogen absorption mechanism could be useful for hydrogen-free machining or for hydrogen-free hydro forming. We suggest that liquid that does not contain hydrogen should be used replacing oil used normally.

CONCLUSION

Heavy hydrogen absorption occurs during standard CBP and the hydrogen comes from the water used in the CBP. We have developed hydrogen-free CBP using hydrogen-free liquid. The combination of the hydrogen-free CBP and CP is a way without causing hydrogen problem. Combination of the hydrogen-free CBP and EP with our polishing liquid mixture resulted in no hydrogen Q-disease. We have successfully found hydrogen-free processes.

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